

Electronic Supplementary Information (ESI)

Binder-free hierarchical zeolite pellets and monoliths derived from ZSM-5@LDH composites for bioethanol dehydration to ethylene

Chadatip Rodaum,^a Sorasak Klinyod,^a Watinee Nunthakitgoson,^a Peeranat Chaipornchalem,^a Nathawoot Liwathananukul,^a Ploychanok Iadrat,^b and Chularat Wattanakit*^a

^aDepartment of Chemical and Biomolecular Engineering, School of Energy Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand.

^bSchool of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand.

E-mail: chularat.w@vistec.ac.th

Experimental section

Materials: For zeolite synthesis, aluminum isopropoxide ($C_9H_{12}AlO_3$: Sigma-Aldrich, $\geq 98.0\%$); tetraethyl orthosilicate (TEOS: Sigma-Aldrich), sodium fluoride (NaF: Carlo Erba), and tetra (n-butyl) ammonium hydroxide (TBAOH: 40 wt% in H_2O , Leonid Chemicals) were used as precursors for zeolite synthesis without further purification. After obtaining the synthesized zeolites, aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$: Sigma-Aldrich), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$: Sigma-Aldrich), sodium carbonate (Na_2CO_3 : Sigma-Aldrich), and sodium hydroxide anhydrous pellets (NaOH: Carlo Erba reagent) were used to synthesize the zeolite@LDH composites further.

Synthesis of powder hierarchical ZSM-5 nanosheets with Si/Al of 20 (Z5-NS): The hierarchical ZSM-5 nanosheets with the Si/Al of 20 were prepared via a hydrothermal process using the precursor with the molar composition of $60SiO_2$: $1.2Al_2O_3$: $18TBAOH$: $3NaF$: $240EtOH$: $600H_2O$. In a typical procedure, aluminum isopropoxide (0.32 g) was dissolved in an alkaline solution containing 0.09 g of sodium fluoride and 2.32 g of DI water. The prepared mixture was then stirred at room temperature to obtain a homogenous sodium aluminate solution. Subsequently, the prepared solution was dropped into the mixture containing 8.6 g of TEOS and 8.10 g of TBAOH, which was vigorously stirred at room temperature for 24 h. After that, the obtained gel was transferred into the Teflon-lined hydrothermal autoclave for crystallization at $130\text{ }^\circ\text{C}$ for 2 days with a ramp rate of $3\text{ }^\circ\text{C}/\text{min}$. The solid product was collected and washed with DI water until the pH of the filtrate is neutral. Finally, the sample was dried overnight at $100\text{ }^\circ\text{C}$ and calcined at $550\text{ }^\circ\text{C}$ for 8 h with a ramp rate of $4.3\text{ }^\circ\text{C}/\text{min}$. Prior to the catalytic testing of the prepared samples in bioethanol dehydration, the catalyst was sieved to a small particle size in the range of $425\text{--}850\text{ }\mu\text{m}$ and denoted as Z5-NS.

Synthesis of powder Z5-NS@LDHs composites: The powder Z5-NS@LDHs composite was prepared following the literature procedure with some modifications.^{1, 2} In the general procedure, the solution containing 0.62 g of $Mg(NO_3)_2 \cdot 6H_2O$, 0.45 g of $Al(NO_3)_3 \cdot 9H_2O$, and 48 mL of DI water was prepared and added into the mixture containing 0.5 g of zeolite (Na^+ form) and 0.26 g of Na_2CO_3 in 100 mL with the dropping rate of 1 mL min^{-1} . In addition, to adjust the pH of the prepared solution (pH=10), 1M NaOH was added to the above-mentioned obtained solution. After stirring the mixture for an hour, the obtained solid was collected and washed

with DI water. Then, the solid product was treated using acetone as solvent via Aqueous Miscible Organic Solvent Treatment Method (AMOST). Finally, the final powder product was dried in an oven overnight. The obtained composites are denoted as Z5-NS@LDHs.

Preparation of the binder-free Z5-NS pellets: Prior to the catalyst-forming process, the ion exchange process was carried out to transform as-synthesized Z5-NS@LDHs composites into acidic catalysts. Generally, 1 g of a composite sample was dispersed in the 100 mL of 0.1M NH_4Cl solution at 80 °C for 2 h repeated by three consecutive cycles. Subsequently, the composite in ammonium form (NH_4^+) was obtained. Regarding the catalyst-forming process, 2.5 wt% of methylcellulose was mixed with DI water, and the catalysts were obtained after an ion exchange process without adding any extra binders. Subsequently, the obtained paste was filled into the standard extrusion equipment, and then it was pressed to form a cylindrical-shaped catalyst. Subsequently, the obtained extruded catalysts were dried in an oven and then calcined at 550 °C for 4 h with the ramp rate of 4.3 °C/min to remove methylcellulose to obtain an acidic catalyst, which is denoted as the BF-Z5-NS pellets containing an aspect ratio (length: diameter) of 3:1, where the diameter is 2 mm.

In addition, the catalysts with spheres and pellets with an aspect ratio of 2:1 were prepared and denoted as the BF-Z5-NS sphere and the BF-Z5-NS(2:1) pellets, respectively.

Moreover, to confirm the complete removal of methylcellulose after calcination at 550 °C, FTIR experiments of BF-Z5-NS pellets before and after calcination were carried out. As shown in Fig. S1, there is no characteristic band in the range of 3000-2800 cm^{-1} , which corresponds to C-H stretching of methylcellulose in the calcined BF-Z5-NS pellets, whereas the corresponding peaks can be observed in the case of the sample before calcination. It is, therefore, reasonable to conclude that the calcination at 550 °C can completely remove the methylcellulose.

Apart from preparing extruded catalysts by a traditional extrusion technique, the new 3D printing technology has been applied in the catalyst-shaping process. Typically, the catalyst paste was prepared by utilizing the above-mentioned similar procedure. In general, 97.5 wt% of catalyst was mixed with 2.5 wt% of methylcellulose and DI water to obtain the optimized viscosity of the paste. Subsequently, the obtained mixture was transferred into a 20 mL syringe equipped with a nozzle of 1.2 mm in diameter for the injection process. The

3D-printed catalyst was obtained using the modified 3D printer, as shown in Fig. S7. The obtained paste was injected onto the hot plate layer-by-layer to form a designed monolith. After that, the monolith sample was dried and calcinated at 550 °C for 4 h. The obtained extruded catalyst monolith formed by using a 3D printing technique is denoted as the BF-Z5-NS-3D.

Preparation of physical mixture between the isolated Z5-NS and the LDHs pallets (phy_Z5-LDHs): After the preparation of 22 wt% of LDHs mixed with the Z5-NS (H⁺ form) powder by using the mortar, the catalyst-forming process of the prepared physical mixture powder was carried out using the same procedure as the BF-Z5-NS pellets as stated above.

Preparation of Z5-NS/MgAlO_x pallets: Before the catalyst-forming process, the MgO and Al₂O₃ supported on Z5-NS powder (H⁺ form) were prepared by using the normal impregnation method. Typically, the Z5-NS (H⁺ form) catalyst was added into a solution containing a precise amount of Mg(NO₃)₂ · 6H₂O and Al(NO₃)₃ · 9H₂O in 10 ml of DI water. After stirring the mixture for 2 h, the sample was collected and dried at 100 °C overnight to obtain the Z5-NS/MgAlO_x powder. Subsequently, the prepared powder was formed into the pellets by using the same procedure as the BF-Z5-NS pellets. The composition of all the synthesized materials is shown in Table S1.

Characterizations: X-ray diffraction (XRD) patterns were recorded on the Bruker D8 ADVANCE instrument using CuK α radiation (40 kV, 40 mA) in the 2 θ range of 5° to 60° with 0.02° of step sizes. Scanning Electron Microscopy (SEM) images were performed on JEOL JSM-7600F (at 2 kV) microscope to observe the morphologies of all the synthesized catalysts. Moreover, Transmission Electron Microscopy (TEM) images, Scanning Transmission Electron Microscopy (STEM), and Energy Dispersive X-ray Spectroscopy (EDS) elemental mapping images were obtained using a JEOL JEM-2100 microscope at 200 kV to investigate the morphology and elemental distribution of all the prepared catalysts. The composition of synthesized catalysts was measured by X-ray Fluorescence (XRF) spectrometry technique carried out on a Bruker AXS S4 Pioneer instrument with a 75 μ m Be window and using the Rh X-ray tube. In terms of the analysis of textural properties, it was performed on a Micromeritics ASAP 2060 instrument at -196 °C, and the catalysts were pretreated at 300 °C for 24 h under vacuum conditions to remove moisture and impurities before the measurement. The Brunauer–

Emmett–Teller (BET) theory was used to calculate the specific surface area (S_{BET}). In addition, micropore volume (V_{micro}), micropore area (S_{micro}), and external surface area (S_{ext}) were determined by the t -plot method. To investigate the mechanical strength of prepared samples, the multi-functional digital force gauge (IPX-804) was applied. The tool contains the loaded cell in the range of 0-20 N with an accuracy of $\pm 0.5\%$. Regarding the acid-base properties of all the prepared catalysts, temperature-programmed desorption of ammonia (NH_3 -TPD) and carbon dioxide (CO_2 -TPD) were carried out on the Belcat II chemisorption instrument equipped with thermal conductivity detectors (TCD). Before the measurement, a catalyst (0.05 g) was pretreated at 300 °C for 1 h under 30 mL min^{-1} of He flow, and then the ammonia or carbon dioxide adsorption was performed at 100 °C for 30 min. Subsequently, the samples were heated from 100 to 800 °C with a heating rate of 10 °C min^{-1} to record the temperature desorption profile. To investigate the type of acid sites, the diffuse reflectance infrared fourier transform (DRIFTS) spectra of pyridine adsorption were measured at 40 °C by using Mercury Cadmium Telluride (MCT) detector on a Bruker Invenio R instrument with a 4 cm^{-1} of scanning resolution. The pyridine was adsorbed at 40 °C under vacuum conditions for 1 h after the pretreatment process of a catalyst for 2 h at 500 °C under N_2 flow. Afterward, the physisorbed pyridine molecules were removed under vacuum conditions. Finally, the FTIR spectra were recorded at 150 °C. In addition, the spectra were normalized by dividing with the area of the overtone in the region of 1750 to 2100 cm^{-1} .

Catalytic test: The catalytic performance of bioethanol dehydration was studied using a fixed-bed reactor under atmospheric pressure at 350°C. Initially, a catalyst was packed into the middle of the reactor tube and pretreated under nitrogen flow (5 mL min^{-1}) at 350 °C for 3 h. After that, bioethanol was introduced into the reactor at 350°C with a weight hourly space velocity (WHSV) of 5 h^{-1} . The reaction mixture was analyzed by online gas chromatography (Agilent 7820B GC) equipped with an FID detector using a PARABOND-Q capillary column. In addition, the mass balance was calculated in the range of $99.4 \pm 2.1\%$, and the standard error of the mean (s.e.m) of ethylene yield was 0.95% estimated by Eq. (1) and Eq. (2), respectively. Moreover, the bioethanol conversion and product selectivity were calculated by Eq. (3) and Eq. (4), respectively.

$$\text{Mass balance (\%)} = \frac{\text{Summation of mass of products} + \text{mass of remaining reactant}}{\text{mass of initial reactant}} \times 100\% \quad (1)$$

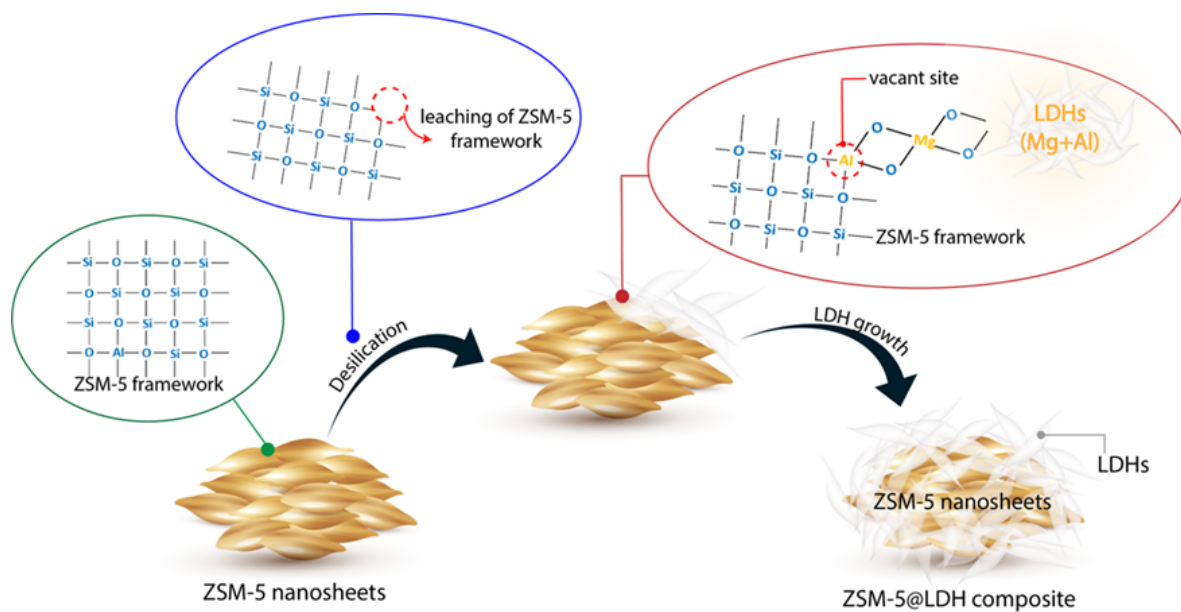
$$s. e. m = \frac{s}{\sqrt{n}} \quad (2)$$

where s and n refer to standard deviation and the number of experiments, respectively.

$$\text{Ethanol conversion (\%)} = \left(\frac{n_{EtOH,i} - n_{EtOH,t}}{n_{EtOH,i}} \right) \times 100\% \quad (3)$$

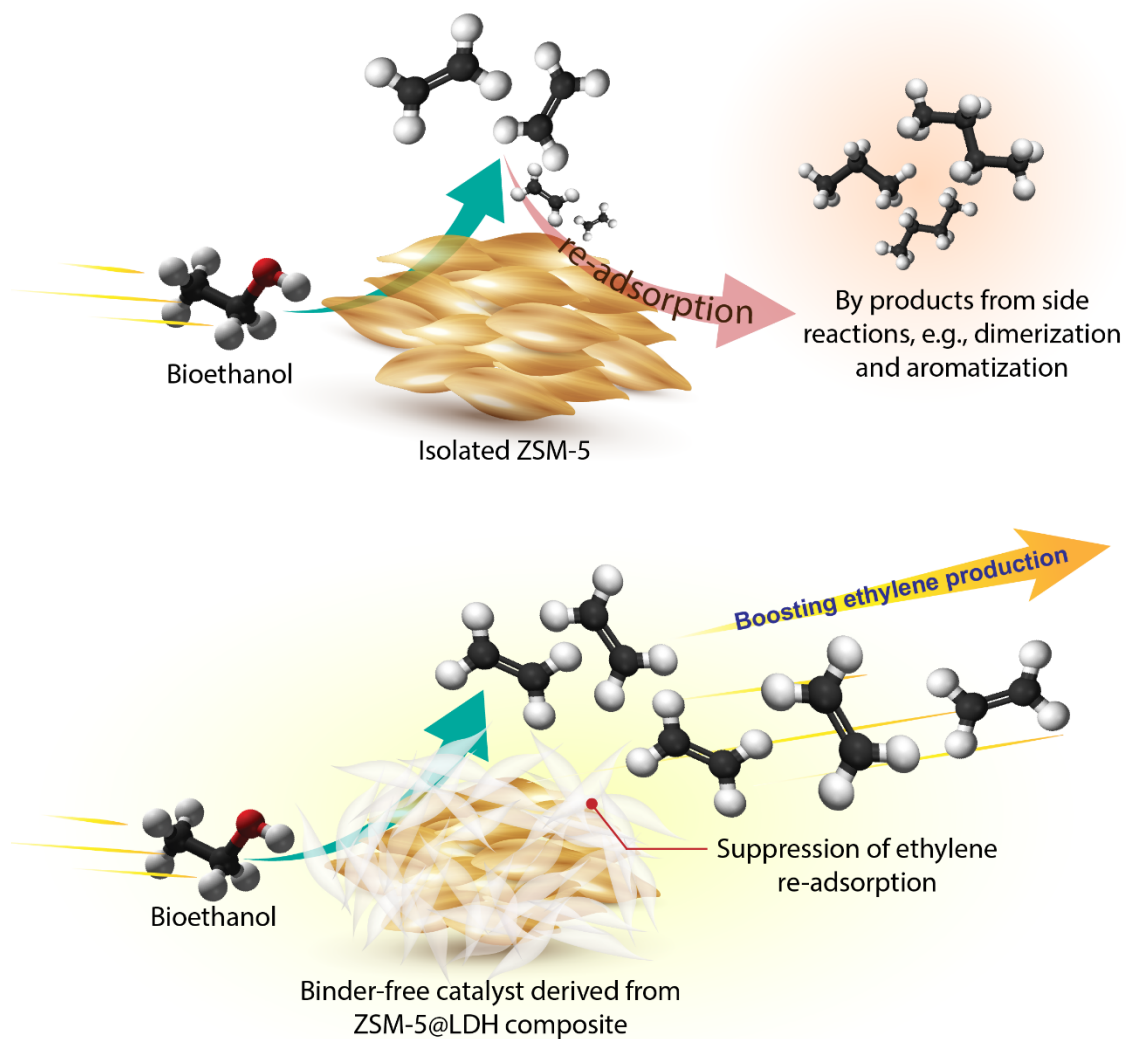
$$\text{Product selectivity (\%)} = \left(\frac{n_i}{\Sigma n} \right) \times 100\% \quad (4)$$

where $n_{EtOH,i}$, $n_{EtOH,t}$, n_i , and Σn refer to the number of moles of ethanol at the initial time, the number of moles of ethanol at a certain time, the number of moles of the desired product i , and the total number of moles of all the products, respectively.



Scheme S1 illustration of the fabrication of the Z5-NS@LDHs composite.

For the first step of the fabrication of the Z5-NS@LDHs composite, the zeolite was dispersed into the alkaline solution, resulting in the desilication of zeolite. Therefore, some parts of the silicon in the zeolite framework were leached out and generated the vacant sites on the zeolite surfaces. After that, the Al in the LDHs precursors was inserted in that vacant site, acting as an active site for LDHs nucleation. Finally, the LDHs were grown on the zeolite surfaces to obtain the ZSM-5@LDH composite.



Scheme S2. illustration of the advantage of the synergistic effect of binder-free catalyst derived from ZSM-5@LDH composite compared to isolated ZSM-5.

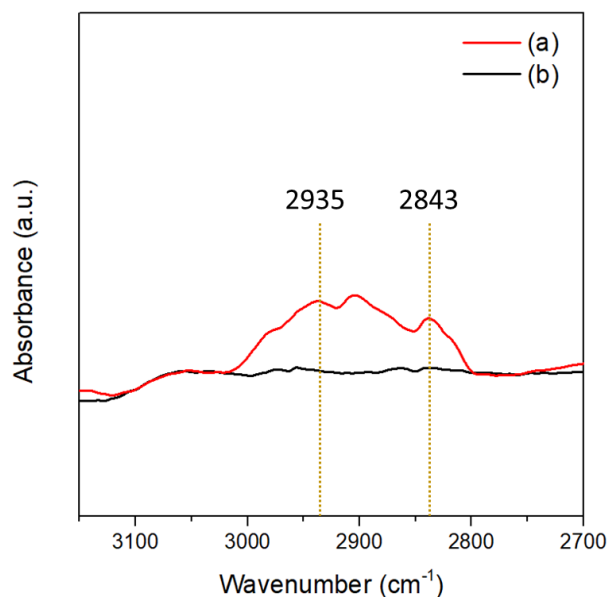


Fig. S1 FTIR spectra of BF-Z5-NS pellets (a) before and (b) after calcination at 550°C.

There is no characteristic band in the range of 3000-2800 cm⁻¹, which corresponds to C-H stretching of methylcellulose in the calcined BF-Z5-NS pellets, whereas the corresponding peaks can be observed in the case of the sample before calcination. It is, therefore, reasonable to conclude that the calcination at 550 °C can completely remove the methylcellulose.

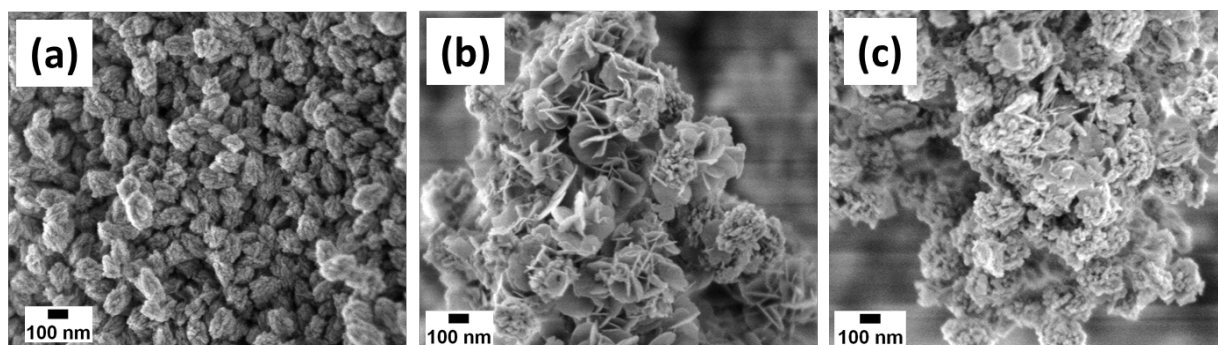


Fig. S2 SEM images of different prepared materials: (a) Z5-NS, (b) Z5-NS@LDHs, and (c) BF-Z5-NS pellets (the sample was crushed into powder before the measurement).

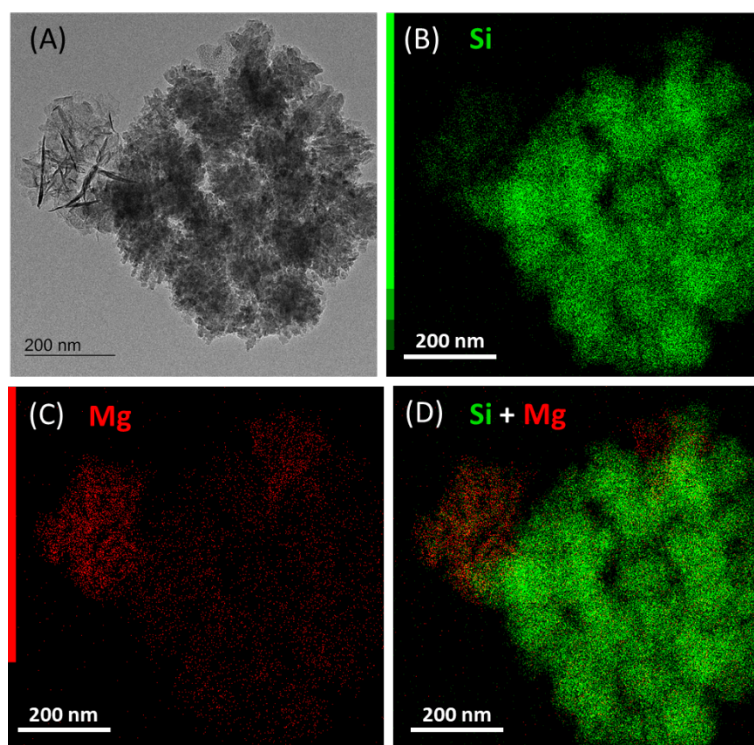


Fig. S3 (A) TEM image and (B-D) STEM and EDS elemental mapping images of physical mixture between the isolated Z5-NS and the LDHs pellets (phy_Z5-LDHs).

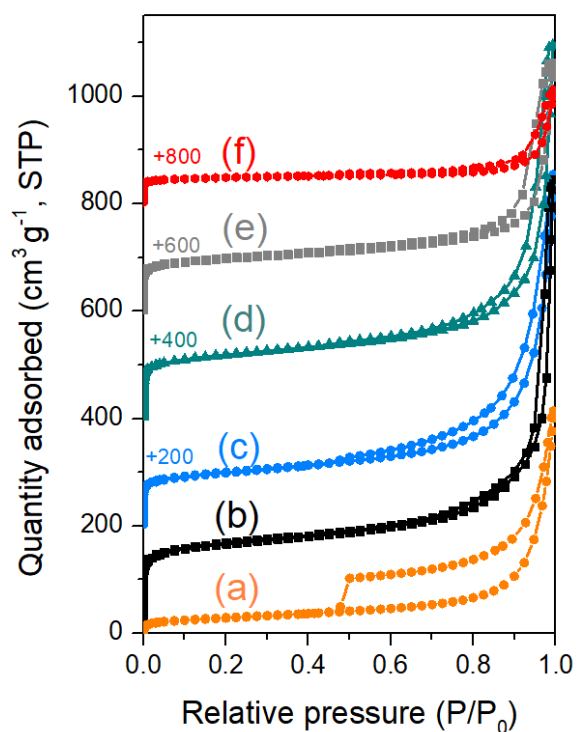


Fig. S4 N₂ adsorption/desorption isotherms of (a) calcined LDHs, (b) Z5-NS, (c) Z5-NS@LDHs, (d) BF-Z5-NS pellets, (e) phy_Z5-LDHs pellets, and (f) Z5-NS/MgAlO_x (imp).

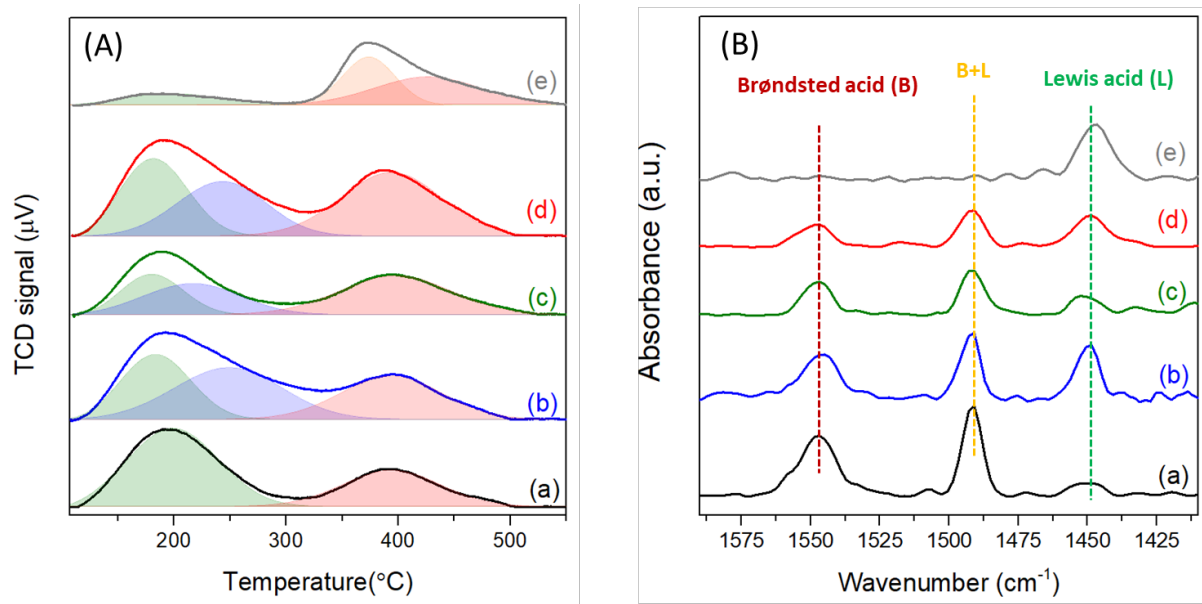


Fig. S5 (A) NH₃-TPD profiles and (B) DRIFTS spectra of adsorbed pyridine of (a) Z5-NS, (b) BF-Z5-NS pellets, (c) phy_Z5-LDHs pallets, (d) Z5-NS/MgAlO_x(imp) pallets, and (e) calcined LDHs.

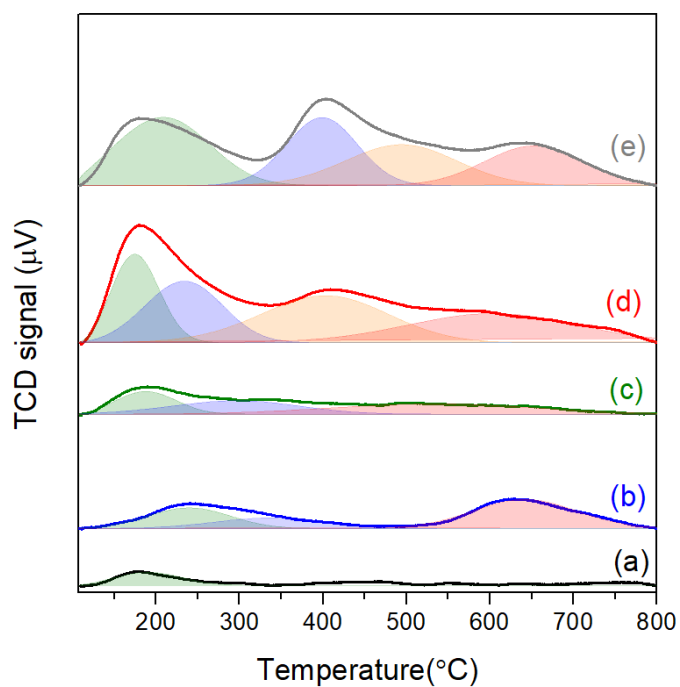


Fig. S6 (A) CO₂-TPD profiles of (a) Z5-NS, (b) BF-Z5-NS pellets, (c) phy_Z5-LDHs pellets, (d) Z5-NS/MgAlO_x(imp) pallets, and (e) calcined LDHs.

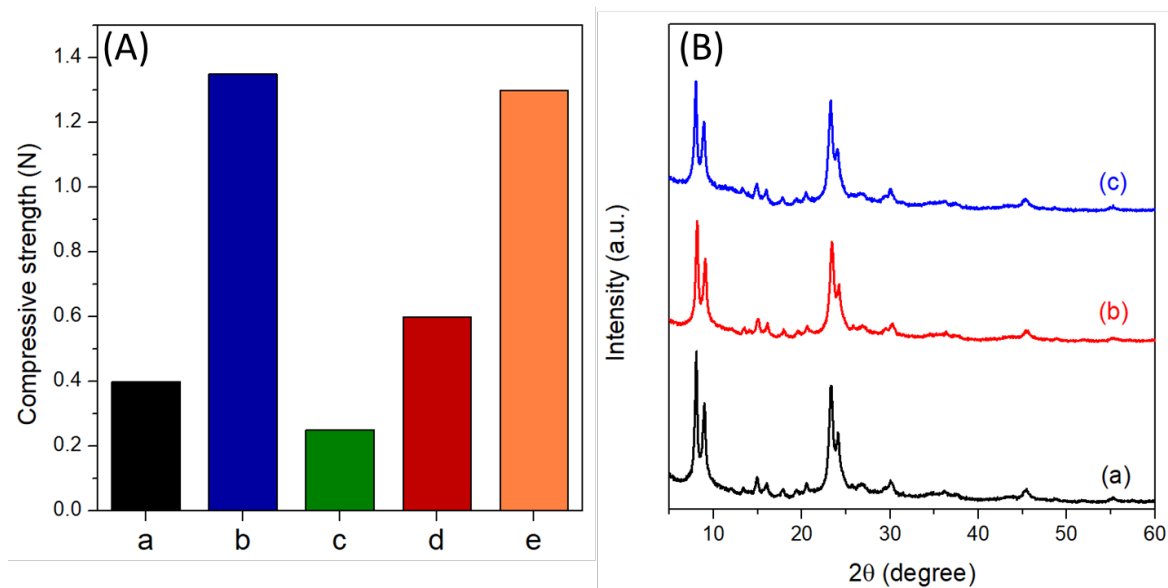


Fig. S7 (A) Mechanical strength of (a) Z5-NS without binder, (b) BF-Z5-NS pellets, (c) phy_Z5-LDHs pellets, (d) Z5-NS/MgAlO_x(imp) pallets, and (e) Z5-NS with 22% wt. of commercial binder (all tests contain an accuracy of $\pm 0.5\%$), and (B) XRD patterns of (a) the binder-free catalysts (BF-Z5-NS) before the thermal stability testing, (b and c) the BF-Z5-NS pellets, and the BF-Z5-NS-3D after the thermal stability testing. (Testing condition: 500 °C for 12 h under N₂ flow).

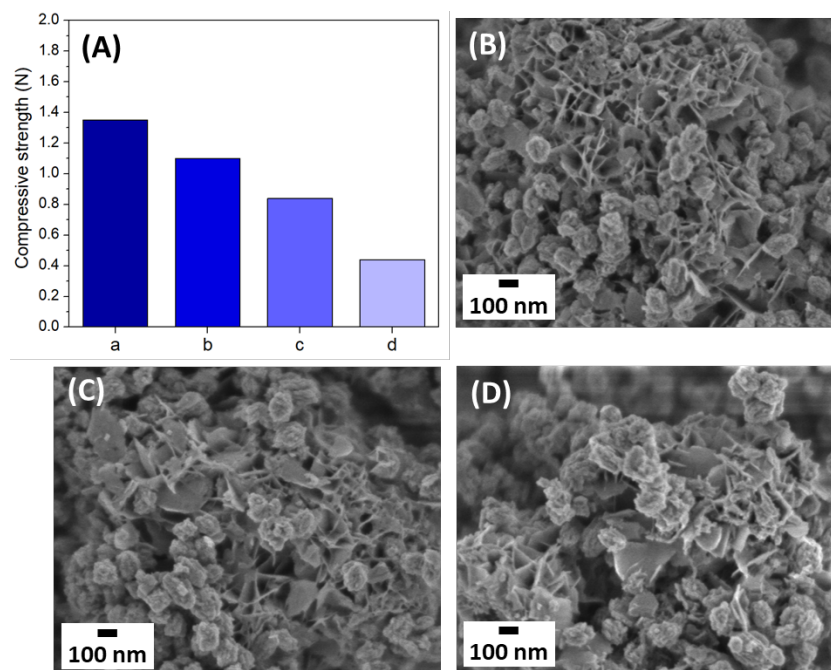


Fig. S8 (A) Mechanical strength of BF-Z5-NS catalyst after hydrothermal stability test at different temperatures: (a) before testing, (b) 250 °C, (c) 350 °C, and (d) 450 °C and SEM images of BF-Z5-NS after hydrothermal testing at (B) 250 °C, (C) 350 °C and (D) 450 °C.

(Hydrothermal stability test: the BF-Z5-NS pallet (0.25 g) was heated at the desired temperatures (250, 350, and 450°C) under N_2 flow of 40 mL min^{-1} in the fixed-bed reactor. After reaching the required temperature, 50 mL min^{-1} of inert gas containing 5 vol% of H_2O was introduced into the reactor for 2 h.)

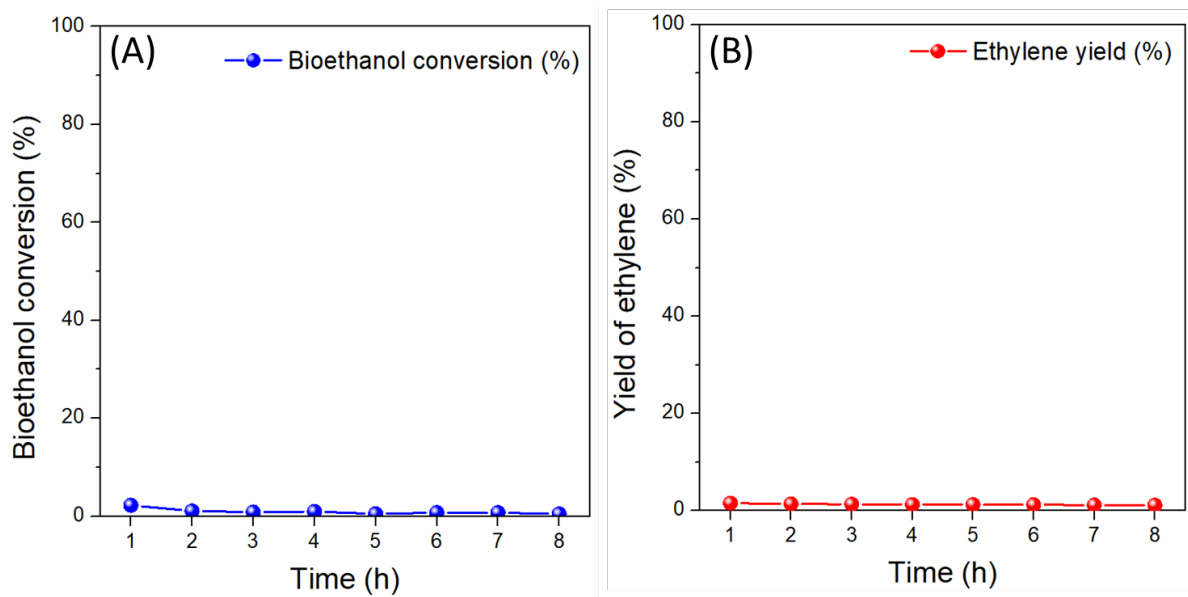


Fig. S9 (A) Catalytic activity as a function of time-on-stream (TOS) of the blank test without a catalyst and (B) Yield of ethylene as a function of time-on-stream over calcined LDHs (Reaction condition: Temperature= 350 °C, WHSV = 5 h⁻¹, and P = 1 atm).



Fig. S10 Photograph of BF-Z5-NS pellets by using a traditional extrusion tool for a catalyst-forming process.

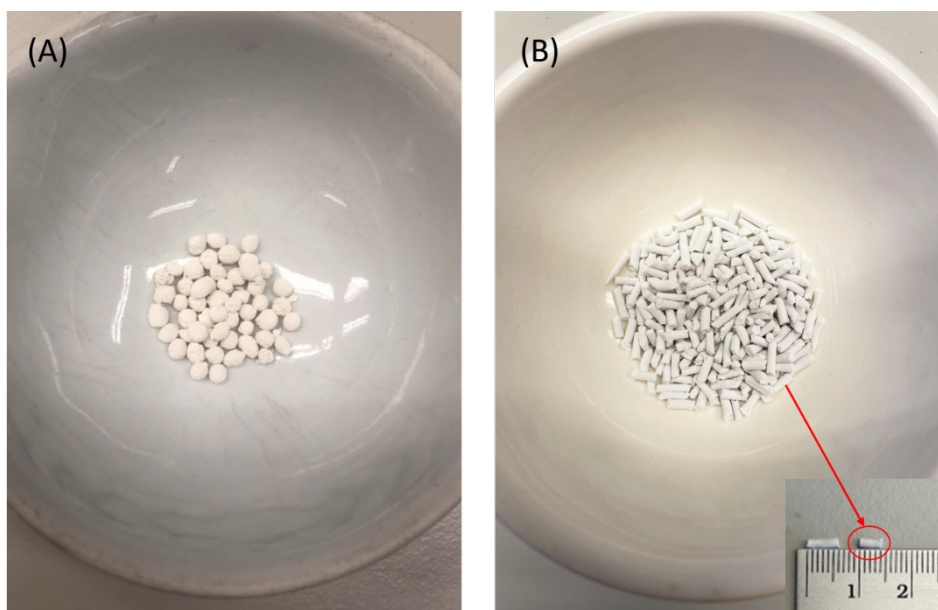


Fig. S11 Photograph of (A) BF-Z5-NS spheres, and (B) BF-Z5-NS(2:1) pellets by using a traditional extrusion tool for a catalyst-forming process.

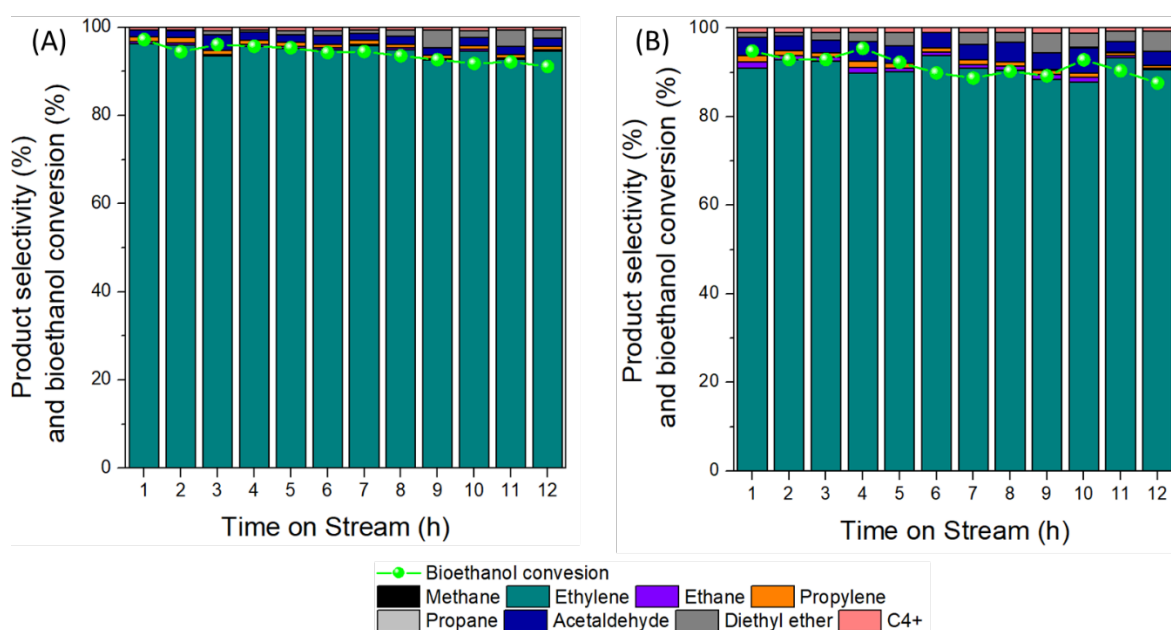


Fig. S12 Catalytic activity as a function of time-on-stream (TOS) upon bioethanol dehydration over the (A) BF-Z5-NS spheres and (B) BF-Z5-NS(2:1) pellets (Reaction condition: Temperature= 350 °C, WHSV = 5 h⁻¹, P = 1 atm).

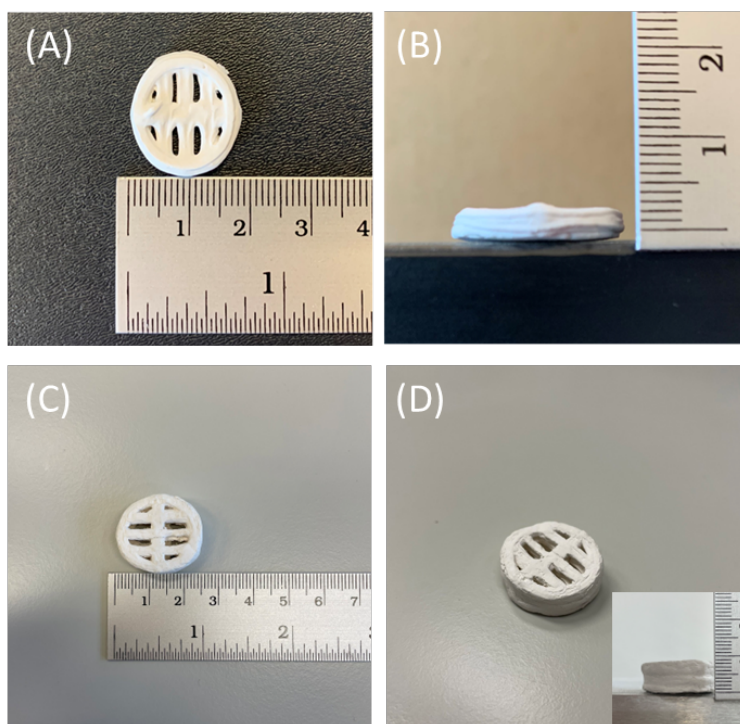


Fig. S13 Photograph of the BF-Z5-NS-3D prepared by using a 3D printing technology for the catalyst-forming process: (A and B) BF-Z5-NS-3D with four-layer and (C and D) BF-Z5-NS-3D with eight-layer.

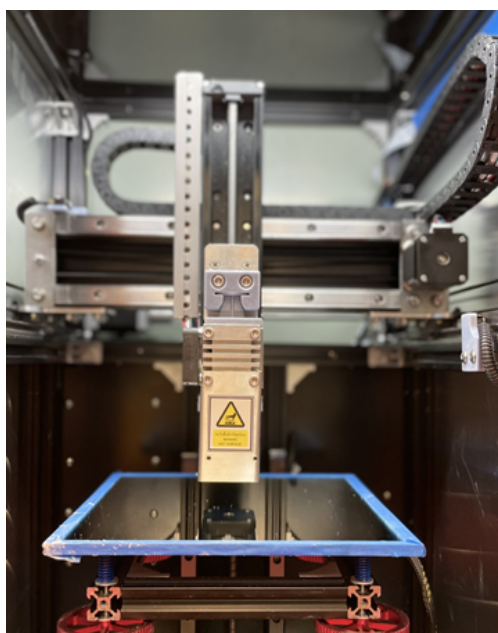


Fig. S14 Photograph of the modified 3D printer machine for the catalyst-forming process.

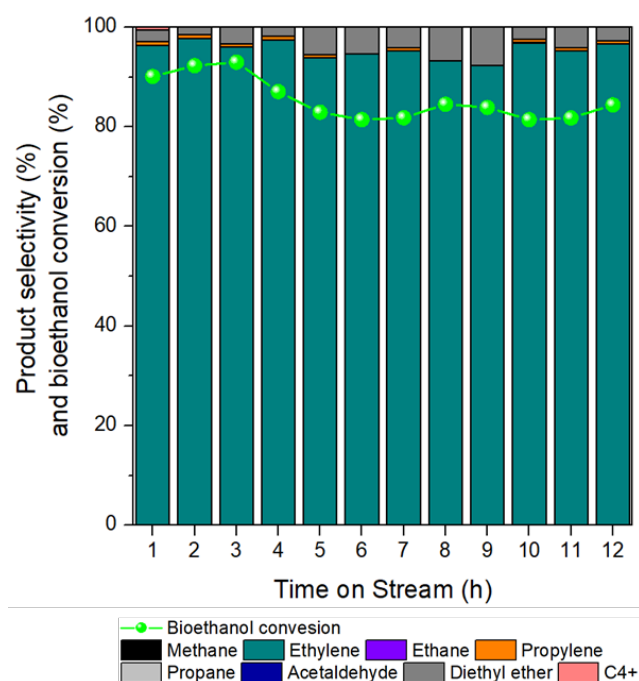


Fig. S15 Catalytic activity as a function of time-on-stream (TOS) upon bioethanol dehydration over the BF-Z5-NS-3D (Reaction condition: Temperature= 350 °C, WHSV = 5 h⁻¹, P = 1 atm).

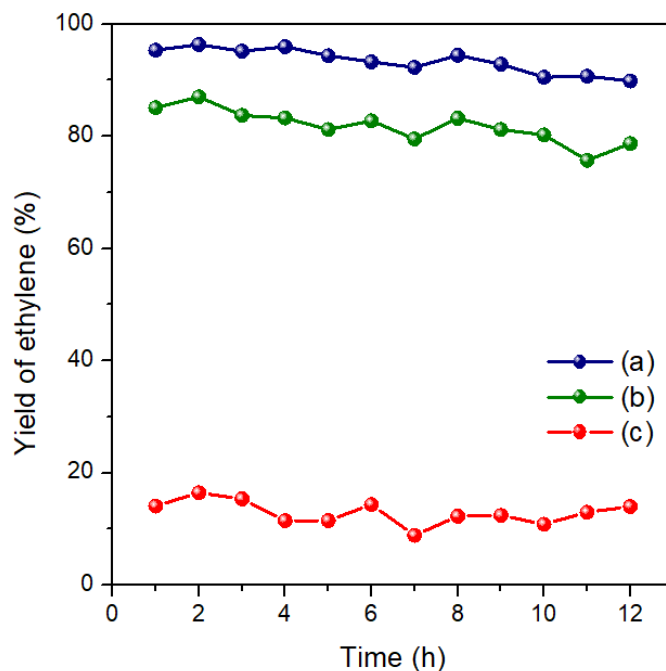


Fig. S16 Yield of ethylene as a function of time-on-stream (TOS) upon bioethanol dehydration at 350 °C over different catalysts: (a) BF-Z5-NS pellets, (b) phy_Z5-LDHs pellets, and (c) Z5-NS/MgAlO_x pellets.

Table S1. The composition of synthesized catalysts obtained by XRF measurements.

Sample	SiO ₂ (wt%)	Al ₂ O ₃ (wt%)	MgO (wt%)	LDH contents ^[a] (wt%)
Z5-NS	96.1	3.9	0	-
BF-Z5-NS pellets	74.3	12.9	12.8	22%
phy_Z5-LDHs pallets	75.6	10.9	13.5	22%
Z5-NS/MgAlO _x (imp)	73.9	12.6	13.5	-

^[a] Data was calculated from the XRF results.

Table S2. Textural properties of all the related materials.

Catalyst	S _{BET} ^a (m ² g ⁻¹)	S _{micro} ^b (m ² g ⁻¹)	S _{ext} ^c (m ² g ⁻¹)	V _{total} ^d (cm ³ g ⁻¹)	V _{micro} ^e (cm ³ g ⁻¹)	V _{meso} ^f (cm ³ g ⁻¹)
Z5-NS	625	470	155	0.54	0.19	0.35
Z5-NS@LDHs	370	221	149	0.51	0.09	0.42
BF-Z5-NS pellets	436	282	154	0.47	0.12	0.35
phy_Z5-LDHs pallets	367	258	109	0.32	0.10	0.22
Z5-NS/MgAlO _x pallets	183	153	30	0.14	0.06	0.08
Calcined LDHs	106	-	-	0.28	-	-

^a S_{BET} (BET specific surface area); ^b S_{micro} (micropore surface area); ^c S_{ext} (external surface area) obtained by *t*-plot method;

^d V_{total} (total pore volume); ^e V_{micro} (micropore volume) obtained by *t*-plot method; ^f V_{meso} (mesopore volume) = V_{total} - V_{micro};

Table S3. The number of total acid sites, the ratio of Brønsted acid sites (B) to Lewis acid sites (L), and Brønsted acid density of all the synthesized catalysts obtained by DRIFTS of pyridine adsorption experiments.

Sample	Weak acid sites ^a (mmol g ⁻¹)	Medium acid sites ^a (mmol g ⁻¹)	Strong acid sites ^a (mmol g ⁻¹)	Total acid sites ^a (mmol g ⁻¹)	Brønsted acid B/L ^b	Brønsted acid density ^c (mmol g ⁻¹)
Z5-NS	0.23	-	0.12	0.35	5.8	0.30
BF-Z5-NS monolith	0.14	0.18	0.15	0.47	0.8	0.21
phy_Z5-LDHs pallets	0.08	0.09	0.15	0.32	1.8	0.20
Z5-NS/MgAlO _x pallets	0.16	0.14	0.19	0.49	0.6	0.19
Calcined LDHs	0.04	-	0.18	0.22	0	0

^a The acidity amount was measured and calculated by NH₃-TPD measurements; ^b Ratio of B/L was obtained from DRIFTS spectra of pyridine adsorption; ^c Data were calculated from NH₃-TPD experiment and DRIFTS spectra of pyridine adsorption

Table S4. The number of total basic sites of all the synthesized catalysts obtained by CO₂-TPD experiments.

Sample	Total basic sites (mmol g ⁻¹)
Z5-NS	0.03
BF-Z5-NS pellets	0.20
phy_Z5-LDHs pallets	0.18
Z5-NS/MgAlO _x pallets	0.67
Calcined LDHs	0.68

Table S5. Textural properties of all BF-Z5-NS materials with different shapes and sizes.

Catalyst	S _{BET} ^a (m ² g ⁻¹)	S _{micro} ^b (m ² g ⁻¹)	S _{ext} ^c (m ² g ⁻¹)	V _{total} ^d (cm ³ g ⁻¹)	V _{micro} ^e (cm ³ g ⁻¹)	V _{meso} ^f (cm ³ g ⁻¹)
BF-Z5-NS pellets	436	282	154	0.47	0.12	0.35
BF-Z5-NS spheres	390	235	155	0.47	0.10	0.37
BF-Z5-NS(2:1) pellets	418	281	137	0.44	0.12	0.32

^a S_{BET} (BET specific surface area); ^b S_{micro} (micropore surface area); ^c S_{ext} (external surface area) obtained by *t*-plot method; ^d V_{total} (total pore volume); ^e V_{micro} (micropore volume) obtained by *t*-plot method; ^f V_{meso} (mesopore volume) = V_{total} - V_{micro}.

References

- 1 C. Chen, C. F. H. Byles, J.-C. Buffet, N. H. Rees, Y. Wu and D. O'Hare, *Chem. Sci.*, 2016, **7**, 1457-1461.
- 2 C. Rodaum, A. Thivasasith, D. Suttipat, T. Witoon, S. Pengpanich and C. Wattanakit, *ChemCatChem*, 2020, **12**, 4288-4296.